

Quantum Brownian motion and the Third Law of thermodynamics *

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The quantum thermodynamic behavior of small systems is investigated in presence of finite quantum dissipation. We consider the archetype cases of a damped harmonic oscillator and a free quantum Brownian particle. A main finding is that quantum dissipation helps to ensure the validity of the Third Law. For the quantum oscillator, finite damping replaces the zero-coupling result of an exponential suppression of the specific heat at low temperatures by a power-law behavior. Rather intriguing is the behavior of the free quantum Brownian particle. In this case, quantum dissipation is able to restore the Third Law: Instead of being constant down to zero temperature, the specific heat now vanishes proportional to temperature with an amplitude that is *inversely* proportional to the ohmic dissipation strength. A distinct subtlety of finite quantum dissipation is the result that the various thermodynamic functions of the sub-system do not only depend on the dissipation strength but depend as well on the prescription employed in their definition.

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1. Introduction

The development of the theory of Brownian motion played a pivotal role – and continues to do so – in the development of statistical mechanics and thermodynamics [1,2]. Thermodynamics together with relativity and quantum theory form three pillars on which much of the entire structure of physics rests. Tampering with the axioms in either of those theories is not a good idea; doing so may well lead to contradictions with the other theories. In particular, the field of thermodynamics bears consequences for many branches of physics. Its four laws are well-known [3,4]: the zeroth law

* This work is dedicated to our colleague and friend, Professor Peter Talkner, on the occasion of his 60-th birthday.

guarantees that states of thermal equilibrium exist which can be characterized by a temperature T . The first law provides a balance among the various contributions that make up the internal energy of a system while the second law introduces the concept of thermodynamic entropy S , which notably is extensive and never decreases for a closed physical system. In addition, the second law tells us that there exists an absolute zero of temperature.

The Third Law is attributed to Walther Hermann Nernst (1864-1941) and arose as the result of his seminal idea – being guided by his critical analysis of chemical and electrochemical reactions at lower temperatures – that at low temperatures there occurs for isothermal processes a perfect correspondence between the enthalpy and the Gibbs free energy. Thereby, the approximate rule hypothesized earlier by Marcelin Berthelot and Julius Thomson, becomes a “law” at zero temperature. Nernst announced this result already in his lectures in 1905, terming it “mein Wärmesatz” (my law of heat) [5, 6]. He took this result even further: He also studied *how* fast the difference between the changes in the enthalpy ΔH and the Gibbs free energy ΔG , *i.e.* $\Delta H - \Delta G$ tends to zero [7]. In fact, this difference vanishes faster than linear in temperature implying that the change of entropy itself must vanish at absolute zero. This in turn implies identical, generally vanishing initial slopes for the corresponding quantities ΔH and ΔG as a function of temperature. An elucidating account of the history of the Third Law and the controversies surrounding its acceptance is presented in the books by Dugdale [8] and by Wilks [9]. In its strict form, as given by Max Planck [10], the Third Law reads: The entropy $s = S/N$ per particle approaches at absolute zero a constant value s_0 that possibly depends on the chemical composition of the system. This limiting entropy constant s_0 can generally be set equal to zero.

The Third Law carries prominent consequences for quantum mechanics and the field of low-temperature physics. First, the fact that at absolute zero temperature the isotherm coincides with the isentrope (adiabat) immediately implies that this absolute zero temperature is unattainable by use of a sequence of isothermal and adiabatic reversible operations [11]. Therefore, it has the consequence that the efficiency of a Carnot engine, *i.e.* a heat engine that cyclically operates between two heat baths of different temperatures which are never brought into contact with each other, can never reach 100% for any finite upper temperature. Moreover, the constant value of the entropy at absolute zero is given by the degeneracy g of the N -particle system in the corresponding quantum ground state, *i.e.* $S(T = 0) = k_B \ln g$, where k_B is the Boltzmann constant. The limiting value of the intensive quantity $s_0 = S(T = 0)/N$ in the thermodynamic limit of particle number $N \rightarrow \infty$ will typically be zero, so long as the degeneracy $g = g(N)$ does not grow with N faster than exponentially [12]. A well-known exception is the

case of noninteracting, independent particles carrying a non-vanishing spin I , yielding $s_0 = k_B \ln(2I+1)$ for the limiting entropy per particle. Moreover, the Third Law also implies that thermal quantities such as specific heats, the isobar thermal coefficient of expansion, the isochor coefficient of tension, etc., all approach zero as $T \rightarrow 0$. Likewise, the (magnetic) susceptibility becomes constant as $T \rightarrow 0$, so that the classic Curie law must lose its validity at very small temperatures.

Are there known exceptions of systems not obeying the Third Law? It is known that many classical systems do not obey the Third Law. In particular, noninteracting classical systems with their constant values for the specific heat clearly violate the Third Law. A well-known case is the classical ideal gas for which the entropy S assumes the form $S = N[c_V \ln T + k_B \ln(V/N) + \sigma]$, where V is the volume and σ denotes the entropy constant. It clearly does not fulfill the Third Law because it diverges logarithmically with temperature T for a constant specific heat c_V . Even when we use for c_V the physically relevant low-temperature result, namely that quantum mechanically the specific heat c_V vanishes faster than $\ln T$, we still find a dependence on the particle density which is not compatible with the formulation of Planck. This observation that the classical gas does not obey the Third Law led Nernst to speculate that the classical gases must undergo a “degeneracy”, which has been resolved with the quantum statistics for the ideal Fermi gas and the ideal Bose-Einstein gas, which indeed do obey the Third Law in the strict formulation by Planck.

Are there yet other remaining open problems with the Third Law? Apparent difficulties with the Third Law occur for metastable states that do not necessarily guarantee the sufficiently fast relaxation within a finite time scale towards thermal equilibrium, the latter being a prerequisite for the validity of the Third Law. In this context, glasses provide a system class that can provide detectable deviations from the Third Law at low temperatures which likely are the result of frozen-in ordered excited states that have not yet fully relaxed. According to common wisdom the known deviations from the Third Law will all be cured by quantum mechanics, quantum statistics, and interactions among particles.

In the following we shall investigate the thermodynamic low temperature properties for open quantum systems that are coupled to a heat bath of *finite* dissipation strength. Because both, the thermodynamics of classical open systems and the quantum statistical mechanics of open systems are strictly valid only for systems that are only infinitely weakly coupled to a bath, it is *a priori* not obvious how the Third Law lives up to the sub-system in presence of finite quantum dissipation [13–22]. The effect of the finite coupling of a sub-system to an environment in fact induces several subtleties for quantum Brownian motion [22]. For example, the equilibrium density

matrix is no longer given by its standard canonical form $\rho_S = \exp(-\beta H_S)/Z$ where H_S denotes the system Hamiltonian and $Z = \text{Tr}[\exp(-\beta H_S)]$ is the partition function. Therefore, in clear contrast to the classical case with dissipation, this reduced density matrix becomes also a function of the interaction strength with the environment. This being so, taking a gas of free independent quantum Brownian particles that are coupled to a heat bath with finite dissipation strength, one may speculate that the role of the interactions of the free particle with the abundant bath degrees of freedom will be sufficient to cure the shortcomings stemming from a classical gas of free Brownian particles.

2. Quantum harmonic oscillator revisited

To start out, we first recall the standard results for a single harmonic quantum oscillator that is infinitely weakly coupled to a bath that establishes the temperature T . This situation is reminiscent of the famous treatment of the specific heat of a solid by Albert Einstein in 1907 [23], where he found an exponential suppression of the specific heat as $T \rightarrow 0$. This finding impressed the Berlin school so immensely, in particular Nernst and his collaborators (who in 1910 experimentally confirmed this salient first prediction of quantum theory), that Nernst together with Planck were able to bring the “new Copernicus” [5,6] into the exclusive circle of Berlin physicists in 1913.

2.1. Partition function and entropy

Let us consider an oscillator degree of freedom of mass M and force constant f , *i.e.* its Hamiltonian H_S reads

$$H_S = \frac{p^2}{2M} + \frac{1}{2}fx^2. \quad (1)$$

In terms of the angular frequency $\omega_0^2 = f/M$ the quantum mechanical energy eigenvalues read $E_n = (n + \frac{1}{2})\hbar\omega_0$, yielding for the partition function Z the well-known expression

$$Z = \sum_{n=0}^{\infty} e^{-\beta E_n} = \frac{1}{2 \sinh[\hbar\beta\omega_0/2]} \quad (2)$$

where $\beta = 1/k_B T$ is the inverse temperature.

Using familiar relations we find that the internal energy E reads

$$E = -\frac{\partial}{\partial\beta} \ln(Z) \quad (3)$$

$$= \frac{\hbar\omega_0}{2} + \frac{\hbar\omega_0}{\exp(\hbar\beta\omega_0) - 1} \quad (4)$$

and, correspondingly, the entropy is given by

$$S = k_B \left[\ln(Z) - \beta \frac{\partial}{\partial\beta} \ln(Z) \right] \quad (5)$$

$$= k_B \left[\frac{\hbar\beta\omega_0}{\exp(\hbar\beta\omega_0) - 1} - \ln(1 - \exp(-\hbar\beta\omega_0)) \right]. \quad (6)$$

For low temperatures, $\hbar\beta\omega_0 \gg 1$, the entropy approaches zero like

$$S = \frac{\hbar\omega_0}{T} \exp\left(-\frac{\hbar\omega_0}{k_B T}\right). \quad (7)$$

The specific heat can now be derived either from (3) as

$$C = \frac{\partial E}{\partial T} = -k_B \beta^2 \frac{\partial E}{\partial\beta} \quad (8)$$

or from (5) as

$$C = T \frac{\partial S}{\partial T} = -\beta \frac{\partial S}{\partial\beta}. \quad (9)$$

In both cases, one obtains for the specific heat

$$C = k_B \left(\frac{\hbar\beta\omega_0}{2 \sinh(\hbar\beta\omega_0/2)} \right)^2. \quad (10)$$

Its low-temperature behavior

$$C = k_B \left(\frac{\hbar\omega_0}{k_B T} \right)^2 \exp\left(-\frac{\hbar\omega_0}{k_B T}\right), \quad (11)$$

is not analytic in temperature and corresponds to Einstein's result for the low-temperature behavior of the specific heat of a solid [23]. For high temperatures one finds

$$C = k_B \left[1 - \frac{1}{12} \left(\frac{\hbar\omega_0}{k_B T} \right)^2 + O(T^{-4}) \right]. \quad (12)$$

As this result shows, the specific heat for a free particle cannot simply be obtained by taking the limit $\omega_0 \rightarrow 0$ of the harmonic oscillator. Such a procedure will not properly account for the reduced number of degrees of freedom which within the equipartition theorem will lead to a high-temperature specific heat of only $C = k_B/2$ for the free particle.

3. Quantum harmonic oscillator: The role of quantum dissipation

3.1. Harmonic oscillator coupled to an environment

We now couple the harmonic oscillator of the previous section to an environment consisting of an infinite number of harmonic oscillators forming a heat bath. In contrast to the previous section, the coupling strength will not be kept negligible here. In addition, system and bath are infinitely weakly coupled to a superbath which has the purpose to provide the temperature T .

The total Hamiltonian H does not need to account for the superbath and therefore consists of three parts [15, 16, 18, 22, 24, 25]

$$H = H_S + H_B + H_{SB} \quad (13)$$

where H_S is given by (1), the bath Hamiltonian reads

$$H_B = \sum_{i=1}^{\infty} \left(\frac{p_i^2}{2m_i} + \frac{m_i \omega_i^2}{2} x_i^2 \right) \quad (14)$$

and the coupling is bilinear in the coordinates

$$H_{SB} = -q \sum_{i=1}^{\infty} c_i x_i + q^2 \sum_{i=1}^{\infty} \frac{c_i^2}{2m_i \omega_i^2}. \quad (15)$$

We note that quantum systems that are coupled to an environment of finite strength are rarely exactly solvable. The dissipative quantum oscillator becomes exactly solvable with its bilinear coupling to a bath because of the inherent quadratic structure of the total Hamiltonian in (13). This fact holds true even for the case of time-dependent, parametrically driven dissipative quantum harmonic systems [26, 27].

In order to describe the influence of the environment on the system oscillator, it is sufficient to know the spectral density of bath oscillators defined by [13, 15, 16, 19]

$$J(\omega) = \pi \sum_{i=1}^{\infty} \frac{c_i^2}{2m_i \omega_i} \delta(\omega - \omega_i). \quad (16)$$

For later purposes, we introduce the Laplace transform of the damping kernel, which generally depends on frequency, thereby causing memory-friction [28, 29], *i.e.*,

$$\hat{\gamma}(z) = \frac{1}{M} \int_0^{\infty} \frac{d\omega}{\pi} \frac{J(\omega)}{\omega} \frac{2z}{\omega^2 + z^2}. \quad (17)$$

The important special case of strictly ohmic dissipation is characterized by $J(\omega) = M\gamma\omega$ and $\hat{\gamma}(z) = \gamma$ which leads to a memoryless damping of strength γ .

3.2. Specific heat of a damped harmonic oscillator

We next discuss the specific heat of the damped harmonic oscillator by following two routes. First, we start from the energy E and employ the common relation in (8). As an alternative route we shall in Section 3.3 determine the entropy from the partition function by means of (5) from which (9) allows one to evaluate the specific heat in the case of strictly ohmic damping.

The energy of the damped harmonic oscillator is given by

$$\langle E \rangle = \frac{\langle p^2 \rangle}{2M} + \frac{M}{2} \omega_0^2 \langle q^2 \rangle \quad (18)$$

where the expectation value of an operator O_S acting in the Hilbert space of the system is defined with respect to the canonical density matrix of system plus environment as

$$\langle O_S \rangle = \frac{\text{Tr} [O_S \exp(-\beta H)]}{\text{Tr} [\exp(-\beta H)]}. \quad (19)$$

For ohmic damping, the second moments of position and momentum can be expressed as [15, 30, 31]

$$\langle q^2 \rangle = \frac{\hbar}{M} f_0(T) \quad (20)$$

and

$$\langle p^2 \rangle = M \hbar f_2(T) \quad (21)$$

where we have introduced a temperature-dependent function

$$f_n(T) = \int_{-\infty}^{+\infty} \frac{d\omega}{2\pi} \frac{\gamma \omega^{n+1}}{(\omega^2 - \omega_0^2)^2 + \gamma^2 \omega^2} \coth \left(\frac{\hbar \beta \omega}{2} \right). \quad (22)$$

For $n = 2$, *i.e.* when evaluating $\langle p^2 \rangle$, the integrand decreases only with $1/\omega$ and a finite value can only be obtained by introducing a high-frequency cut-off in the damping kernel $\hat{\gamma}(z)$. However, this divergent term gives rise only to a temperature-independent contribution to $\langle p^2 \rangle$ and thus to the energy (18). When evaluating the specific heat according to (8), this constant term will disappear and a finite result is obtained even for ohmic damping. After some algebra, one finds for the specific heat

$$\frac{C}{k_B} = 1 - \frac{\hbar \beta \gamma}{2\pi} + \lambda_+^2 \psi' (1 + \lambda_+) + \lambda_-^2 \psi' (1 + \lambda_-) \quad (23)$$

where

$$\lambda_{\pm} = \frac{\hbar\beta\omega_0}{2\pi} \left[\frac{\gamma}{2\omega_0} \pm \sqrt{\left(\frac{\gamma}{2\omega_0}\right)^2 - 1} \right] \quad (24)$$

and $\psi'(z)$ is the trigamma function. At low temperatures, the specific heat thus assumes the form

$$\frac{C}{k_B} = \frac{\pi}{3} \frac{\gamma}{\omega_0} \frac{k_B T}{\hbar\omega_0} + \frac{4\pi^3}{15} \frac{\gamma}{\omega_0} \left[3 - \left(\frac{\gamma}{\omega_0}\right)^2 \right] \left(\frac{k_B T}{\hbar\omega_0}\right)^3 + O(T^5). \quad (25)$$

This result differs significantly from the expression (11) in the absence of dissipation. While in the latter case, the presence of an energy gap led to an exponential suppression of the specific heat, we now find a linear increase with temperature. This behavior indicates the existence of a finite density of states even at small excitation energies [32]. Even at high temperatures the effect of dissipation can be detected, albeit in a less spectacular manner. The leading correction in the high-temperature expansion reads

$$\frac{C}{k_B} = 1 - \frac{\hbar\gamma}{2\pi k_B T} + \frac{\hbar^2(\gamma^2 - 2\omega_0^2)}{24(k_B T)^2} + O(T^{-3}). \quad (26)$$

Thus, the leading correction depends on the damping strength γ . This finding is in clear contrast to the behavior of the quantum escape rate [16, 29]: There, the leading quantum correction to the escape rate always enhances the classical result and is *independent* of the dissipation strength.

3.3. Energy versus partition function for a damped harmonic oscillator

Another prescription to obtain the specific heat starts out from the canonical partition function

$$Z = \frac{\text{Tr} [\exp(-\beta H)]}{\text{Tr}_B [\exp(-\beta H_B)]}, \quad (27)$$

where Tr_B denotes the partial trace in the Hilbert space of the bath. In the absence of a system-bath coupling, this expression would correspond to the partition function of the system alone. For a damped harmonic oscillator, the partition function becomes [33]

$$Z = \frac{1}{\hbar\beta\omega_0} \prod_{n=1}^{\infty} \frac{\nu_n^2}{\nu_n^2 + \nu_n \hat{\gamma}(\nu_n) + \omega_0^2} \quad (28)$$

with the Matsubara frequencies $\nu_n = 2\pi n/\hbar\beta$. In view of the divergence for strictly ohmic damping mentioned above, we allow here for a possible frequency dependence of $\hat{\gamma}$.

Following the standard procedure of statistical mechanics, we can obtain the energy from the partition function by means of

$$\langle E \rangle_Z = -\frac{\partial}{\partial \beta} \ln(Z). \quad (29)$$

Inserting (28), one obtains

$$\langle E \rangle_Z = \frac{1}{\beta} \left[1 + \sum_{n=1}^{\infty} \frac{2\omega_0^2 + \nu_n \hat{\gamma}(\nu_n) - \nu_n^2 \hat{\gamma}'(\nu_n)}{\nu_n^2 + \nu_n \hat{\gamma}(\nu_n) + \omega_0^2} \right] \quad (30)$$

which in general differs from the expression

$$\langle E \rangle = \frac{1}{\beta} \left[1 + \sum_{n=1}^{\infty} \frac{2\omega_0^2 + \nu_n \hat{\gamma}(\nu_n)}{\nu_n^2 + \nu_n \hat{\gamma}(\nu_n) + \omega_0^2} \right] \quad (31)$$

obtained by evaluating the integral (22) by residues. The only exception is the special case of strictly ohmic damping where $\hat{\gamma}(\nu_n) = \gamma$ is constant.

This generally non-vanishing difference does not come as a surprise if one only takes a closer look at the partition function (27): The evaluation of (29) yields

$$\begin{aligned} \langle E \rangle_Z &= \langle H \rangle - \langle H_B \rangle_B \\ &= \langle E \rangle + [\langle H_{SB} \rangle + \langle H_B \rangle - \langle H_B \rangle_B] \end{aligned} \quad (32)$$

where the index “B” denotes an average with respect to the bath Hamiltonian H_B only. This result differs from the energy $\langle E \rangle = \langle H_S \rangle$ by the term in the brackets which, generally, vanishes only in the absence of a system-bath coupling. The coincidence between $\langle E \rangle$ and $\langle E \rangle_Z$ for the harmonic oscillator subject to strictly ohmic damping should therefore be considered as exceptional.

Nevertheless, we briefly sketch how one would obtain the specific heat from the partition function because this will give us as a by-product an expression for the entropy of the damped harmonic oscillator. For strictly ohmic damping the product (28) does not converge and in principle a high-frequency cutoff for $\hat{\gamma}$ should be introduced. However, this divergence can again be traced back to an infinite energy shift due to the environmental coupling. We may shift the energy by an arbitrary amount Δ by multiplying the partition function by $\exp(-\beta\Delta)$ without changing the entropy or the specific heat. After performing an appropriate energy shift, we arrive at an expression of the partition function valid even for strictly ohmic damping [34], reading

$$\bar{Z} = \frac{A}{\hbar\beta\omega_0} \left(\frac{2\pi}{\hbar\beta\omega_0} \right)^{\hbar\beta\gamma/2\pi} \Gamma(1 + \lambda_+) \Gamma(1 + \lambda_-), \quad (33)$$

where $\Gamma(z)$ is the gamma function, λ_{\pm} are defined in (24), and A is a constant whose precise value is irrelevant for the following. By virtue of (5) we obtain for the entropy the result

$$S = k_B \left[1 - \ln(\hbar\beta\omega_0) + \frac{\hbar\beta\gamma}{2\pi} + g(\lambda_+) + g(\lambda_-) \right], \quad (34)$$

where we introduced the abbreviation

$$g(z) = \ln[\Gamma(1+z)] - z\psi(1+z) \quad (35)$$

with the digamma function $\psi(z) = \Gamma'(z)/\Gamma(z)$. In the absence of damping, *i.e.* $\gamma = 0$, this reproduces the result (6) for the entropy of an uncoupled harmonic oscillator.

For very low temperatures, the entropy (34) vanishes like

$$S = \frac{\pi}{3} \frac{\gamma}{\omega_0} \frac{k_B^2 T}{\hbar\omega_0} + O(T^3) \quad (36)$$

as required by the Third Law of thermodynamics. By means of (9), the expression (23) for the specific heat is recovered identically.

The low-temperature behavior (36) is in agreement with the expression derived by Ford and O'Connell on the basis of the free energy [35]. For the damped harmonic oscillator these authors found that the entropy vanishes in the limit of zero temperature also for more general forms of the bath density of states.

4. Free quantum Brownian motion coupled to a heat bath: Is the Third Law obeyed at zero temperature?

According to the equipartition theorem the specific heat of a free particle is $k_B/2$. In the limit of an infinite “box” this represents even the correct quantum value, because the classical and the quantum partition function become equal. In view of the fact that the specific heat of an ideal gas thus remains non-zero down to the lowest temperatures, one becomes curious to investigate the specific heat of a free particle coupled to an environment when the coupling strength is not assumed to vanish: Does quantum dissipation help to restore the Third Law?

Free quantum Brownian motion has been addressed in earlier work [36–39] wherein the main focus centered on the role of free quantum diffusion [15]. Interestingly enough, for ohmic dissipation the quantum diffusion remains “classical”, being proportional to time t , except at zero temperature itself, where one finds a logarithmic behavior in time t [36–39]. At finite temperatures this quantum behavior is observable at intermediate times

only [36, 40]. One is thus tempted to conclude that finite quantum dissipation will not be sufficient to cure the classical behavior for the specific heat. Therefore, we shall next investigate the behavior of the specific heat for free quantum Brownian motion in closer detail.

As already mentioned at the end of Section 2.1, simply taking the limit $\omega_0 \rightarrow 0$ in the results for the damped harmonic oscillator is not without problems. We therefore start our calculation from the energy

$$\langle E \rangle = \frac{\langle p^2 \rangle}{2M} = \frac{1}{2\beta} \left[1 + 2 \sum_{n=1}^{\infty} \frac{\nu_n \hat{\gamma}(\nu_n)}{\nu_n^2 + \nu_n \hat{\gamma}(\nu_n)} \right] \quad (37)$$

which can be obtained from the second moment of momentum $\langle p^2 \rangle$ by evaluating the integral (22) by residues. Proceeding as in Section 3.2, one derives the specific heat of the free particle in the presence of strictly ohmic damping

$$\frac{C}{k_B} = \frac{1}{2} - \frac{\hbar\beta\gamma}{2\pi} + \left(\frac{\hbar\beta\gamma}{2\pi} \right)^2 \psi' \left(1 + \frac{\hbar\beta\gamma}{2\pi} \right) \quad (38)$$

which for either $T \rightarrow \infty$ or $\gamma \rightarrow 0$ yields $C = k_B/2$, as expected from the equipartition theorem. On the other hand, for low temperatures the specific heat tends to zero as

$$\frac{C}{k_B} = \frac{\pi}{3} \frac{k_B T}{\hbar\gamma} - \frac{4\pi^3}{15} \left(\frac{k_B T}{\hbar\gamma} \right)^3 + O(T^5) \quad (39)$$

in agreement with the Third Law of thermodynamics. The specific heat (38) together with its linear low-temperature behavior are depicted in the main part of Fig. 1 as full and dashed line, respectively. Temperatures $k_B T \gg \hbar\gamma$ much larger than the damping strength are required in order to restore the classical result $C/k_B = 1/2$.

As the damping strength already serves to set the temperature scale, it is instructive to introduce a cutoff in the density of states (16) of the bath oscillators in order to study how a reduction of the environmental influence changes the dependence of the specific heat on temperature. To this end, we introduce a high-frequency cutoff ω_D by choosing the Drude model where

$$\hat{\gamma}(z) = \frac{\gamma\omega_D}{z + \omega_D}. \quad (40)$$

This environment leads to a specific heat

$$\frac{C}{k_B} = \frac{1}{2} - \frac{\hbar\beta\gamma}{2\pi} \frac{1}{\sqrt{1 - 4\gamma/\omega_D}} \left[z_+ \psi'(1 + z_+) - z_- \psi'(1 + z_-) \right], \quad (41)$$

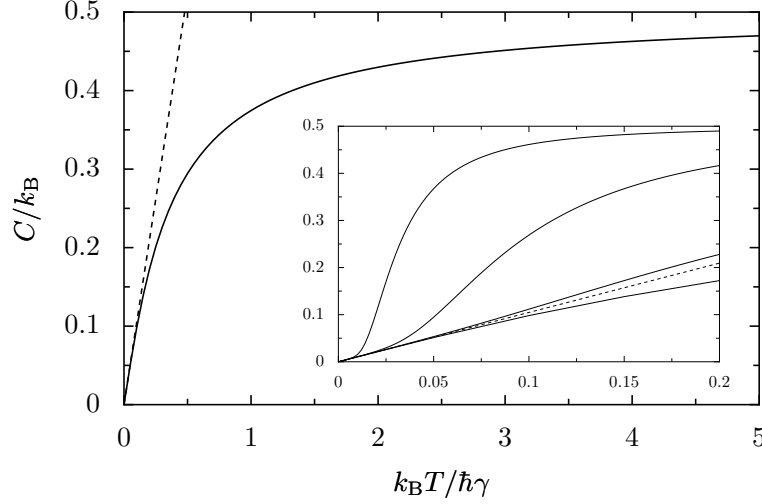


Fig. 1. The specific heat C of a free quantum Brownian particle is shown as a function of the temperature T for strictly ohmic friction of strength γ . The dashed line indicates the linear low-temperature behavior. In the inset, the modification due to a finite cutoff frequency ω_D is depicted for different cutoff scales, $\omega_D/\gamma = 0.01, 0.1, 1$, and ∞ from the upper to the lower full line. The dashed line indicates again the linear low-temperature behavior.

where we have introduced the abbreviations

$$z_{\pm} = \frac{\hbar\beta\omega_D}{4\pi} \left(1 \pm \sqrt{1 - \frac{4\gamma}{\omega_D}} \right). \quad (42)$$

Independently of the value of the cutoff frequency ω_D , the specific heat will go to zero linearly as stated in (39). However, for temperatures larger than the cutoff frequency, the suppression of the specific heat due to the environmental coupling will be ineffective. A reduction of the environment thus tends to restore the classical value of $k_B/2$ for the specific heat. This effect is depicted in the inset in Fig. 1, where the cutoff frequency takes the values $\omega_D/\gamma = 0.01, 0.1, 1$ and ∞ from the upper to the lower curve. The dashed curve represents the linear low-temperature behavior which still dominates at temperatures below $\hbar\omega_D/k_B$. In contrast to many phenomena in quantum dissipation, here an increase of the coupling to the environment does not render the system more classical. On the contrary, a stronger environmental coupling makes the dissipative quantum system behave more quantum mechanically and thus helps to ensure the validity of the Third Law of thermodynamics, *i.e.* the vanishing of the specific heat with decreasing temperatures.

5. Conclusions

With this work we have explored the behavior of the specific heat for a quantum system that is coupled to a heat bath with finite coupling strength. Our findings are contrasted with the Third Law of thermodynamics which generically predicts a vanishing of the specific heat at low temperatures. For a harmonic oscillator the presence of quantum dissipation changes the well-known Einstein-like behavior of an exponentially fast approach towards zero specific heat into a power-law behavior with a slope that increases with increasing coupling strength. Even more intriguing is the behavior for a freely moving quantum particle: While the quantum treatment in absence of dissipation simply coincides with the classical behavior, *i.e.* the specific heat takes a constant value $C = k_B/2$, the role of finite quantum dissipation is able to restore the Third Law, yielding a leading linear temperature dependence. Quite counterintuitively, its approach to the classical value occurs the faster the weaker is the dissipation strength.

In contrast to common quantum statistical mechanics which intrinsically is based on a vanishingly small coupling to the environment, the finite coupling strength between the sub-system and the bath causes some subtleties that must be recognized. As made explicit in Section 3.3, the thermodynamic quantities depend on the procedure invoked in their definition: the commonly used expression based on the partition function provides results that generally do *not* agree with the result obtained from the corresponding quantum expectation value. Interestingly enough, in the strict ohmic limit (*i.e.* in the absence of a high-frequency cutoff) the specific heat for the damped harmonic oscillator does not depend on the prescription employed. For the case of memory friction, however, where a finite cutoff frequency is present, the thermodynamic quantities depend both on the value of this cutoff and the prescription used in their evaluation.

The results obtained for the low-temperature behavior of the specific heat of simple quantum systems are not only of academic interest, but may turn out to be relevant for experiments in nanoscience where one tests the quantum thermodynamics of small systems [41] that are coupled to an environment with a finite coupling strength.

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